(19) Japanese Patent Office (JP)
(12) Publication of Laid-Open Patent Application (A)
(11) Publication Number of Patent Application:
Japanese Patent Laid-Open Publication No. 2002-237463
(P2002-237463A)
(43) Publication Date of Application: August 23, 2002
(51) Int. Cl.$^7$: H01L 21/205, B01J 19/08, C23C 16/503, 16/509, 16/515
Identification Mark
FI: H01L 21/205, B01J 19/08, C23C 16/503, 16/509, 16/515, H
Theme Code (reference): 4G075, 4K030, 5F045, 5F051
Request for Examination: Not requested
Number of Claims: 10
OL
Total 11 pages
Continued to the last page
(21) Application Number:
Japanese Patent Application No. 2001-226885 (P2001-226885)
(22) Date of Filing: July 27, 2001
(31) Priority Application Number:
Japanese Patent Application No. 2000-229322 (P2000-229322)
(32) Priority Date: July 28, 2000
(33) Priority Country: Japan (JP)
(31) Priority Application Number:
Japanese Patent Application No. 2000-369491 (P2000-369491)
(32) Priority Date: December 5, 2000
(33) Priority Country: Japan (JP)
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(54) [Title of the Invention]

Manufacturing Method and Device of Semiconductor Element

(57) [Abstract]

[Problem to be Solved] To provide a method and a device for manufacturing a thin film easily by using a method in which uniform glow discharge plasma is continuously generated under a pressure in the vicinity of atmospheric pressure and a glow discharge plasma treatment is performed stably, when manufacturing a thin film in a manufacturing process of a semiconductor element.

[Means for Solving the Problem] A manufacturing method of a semiconductor element, wherein a material gas is introduced between opposing electrodes under a pressure in the vicinity of atmospheric pressure, and the material gas is changed into glow discharge plasma by applying a pulsed electric field between the opposing electrodes so that a thin film is formed, in a process of forming a laminated body of a semiconductor element.

[Scope of Claims]

[Claim 1] A manufacturing method of a semiconductor element, wherein a material gas is introduced between opposing electrodes under a pressure in the vicinity of atmospheric pressure, and the material gas is changed into glow discharge plasma by applying a pulsed electric field between the opposing electrodes so that a thin film is formed, in a process of forming a laminated body of a semiconductor element.

[Claim 2] A manufacturing method of a semiconductor element according to Claim 1, wherein voltage rise time of the pulsed electric field is 100 μs or less, and the field intensity is in a range of 10 to 1000 kV/cm.

[Claim 3] A manufacturing method of a semiconductor element according to Claim 1 or 2, wherein a solid dielectric is set on an opposing surface of at least one of the opposing electrodes, and a base material is placed between one of the electrodes and the solid dielectric or between the solid dielectrics, so that a thin film is formed on a surface of the base material.

[Claim 4] A manufacturing method of a semiconductor element according to Claim 1 or 2, wherein a solid dielectric vessel provided with a gas outlet is placed on an electrode and an other electrode is provided opposing to the gas outlet, a base material is placed between the gas outlet and the other electrode, and a material gas changed into plasma is discharged continuously from the gas outlet so that a thin film is formed on a surface of the base material.

[Claim 5] A manufacturing method of a semiconductor element according to Claim 1 or 2, wherein a solid dielectric is set on an opposing surface of at least one of the opposing electrodes, and a material gas changed into plasma is sprayed on a base material between one of the electrodes and the solid dielectric or between the solid dielectrics so that a thin film is formed on a surface of the base material.

[Claim 6] A manufacturing method of a semiconductor element according to Claim 1 or 2, wherein a solid dielectric is set on an opposing surface of at least one of the opposing electrodes, and when a material gas changed into plasma is sprayed on a base material between one of the electrodes and the solid dielectric or between the solid dielectrics, the plasma-state gas is selectively induced to a surface of the base material by applying an electric field to the base material, so that a thin film is formed on the surface of the base material.

[Claim 7] A manufacturing device of a semiconductor element comprising a solid dielectric set on an opposing surface of at least one of opposing electrodes and a base material placed between one of the electrodes and the solid dielectric or between the solid dielectrics, wherein a pulsed electric field is applied between the electrodes.

[Claim 8] A manufacturing device of a semiconductor element comprising a ground electrode provided with a solid dielectric vessel having a gas outlet and an other electrode provided opposing to the gas outlet, wherein a material gas is discharged continuously from the gas outlet, and a pulsed electric field is applied between the ground electrode and the other electrode.

[Claim 9] A manufacturing device of a semiconductor element wherein a solid dielectric is set on an opposing surface of at least one of opposing electrodes and a pulsed electric field is applied between the opposing electrodes, and a material gas changed into plasma is discharged continuously from a gas outlet and sprayed on a base material between one of the electrodes and the solid dielectric or between the solid dielectrics, in a vessel having a gas introducing port and the gas outlet.

[Claim 10] A manufacturing device of a semiconductor element according to any one of Claims 7 to 9, wherein rise time and fall time of a pulsed electric field applied between the electrodes are 100 μs or less, and the field intensity is in a range of 10 to 1000 kV/cm.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The present invention relates to a manufacturing method and a manufacturing device of a semiconductor element, to form a thin film laminated body of a semiconductor element by atmospheric pressure plasma CVD.

[0002]
[Prior Art] Usually, the general structure of a semiconductor element comprises a substrate 1, a silicon film 2, a source electrode 3, a drain electrode 4, an interlayer insulator 5, a gate electrode 6, a passivating film (protective film) 7 and the like, as shown in Fig. 1. Here, as a base material, it is formed of a glass substrate, a wafer substrate or the like, and as an electrode, it is formed of metal such as Al and Cu, a metal compound or the like. A passivating film and an interlayer insulator is formed of silicon oxide, silicon nitride, silicon carbide or the like, and a silicon layer is formed of an a-Si layer, and a material such as a-Si doped with P, B, As, Ge and the like.

[0003] A semiconductor element is manufactured by complicated processes as follows: the above-described materials are combined according to the requested function, a base material and the like is cleaned, thin films such as an electrode, an insulating film and a silicon layer are formed thereon, doping, annealing and resist treatments (coating, development, baking, resist removing and the like, for example) are performed, and exposure, development, etching and the like are repeated. In these manufacturing processes, thin film formation such as formation of an insulating film, a protective film, an electrode and a silicon film is important, and a plasma treatment method is mainly used as the formation method.

[0004] As a method of thin film formation, there are low-pressure plasma CVD, atmospheric pressure thermal CVD, vapor deposition, sputtering and the like, generally. As for conventional atmospheric pressure plasma CVD, the gas kind is limited to under a helium atmosphere and the like. For example, a method in which the treatment is performed under a helium atmosphere is disclosed in Japanese Patent Laid-Open Publication No. 2-48626, and a method in which the treatment is performed under an atmosphere of argon and acetone and/or helium is disclosed in Japanese Patent Laid-Open Publication No. 4-74525.

[0005] However, the above-described methods all generate plasma in a gas atmosphere including an organic compound such as helium and acetone, and the gas atmosphere is limited. In addition, helium is expensive, which is industrially disadvantageous. In the case where an organic compound is included, the organic compound itself often reacts with a substance to be treated, so that a desired surface reformulation treatment cannot be performed sometimes.

[0006] Furthermore, with the conventional method, the treatment speed is slow, which is disadvantageous for industrial processes. In addition, in the case of forming a plasma polymer film and the like, the film disintegration speed is higher than the film formation speed, which leads to a problem that a good-quality thin film cannot be

obtained.

[0007]

[Problem to be Solved by the Invention] In view of the above-described problems, the object of the present invention is to provide a method and the device with which a thin film is easily manufactured on a semiconductor element, using a method in which uniform glow discharge plasma is generated continuously under a pressure in the vicinity of atmospheric pressure and a glow discharge plasma treatment is performed stably, when manufacturing a thin film in a semiconductor element manufacturing process.

[0008]

[Means for Solving the Problem] The present inventors studied diligently to solve the above-described problem, and as a result, found out that a thin film can be formed easily by a discharge plasma method which realizes a stable state of discharge under an atmospheric pressure condition, then completed the invention.

[0009] That is, the first invention (the invention of Claim 1) is a manufacturing method of a semiconductor element, wherein a material gas is introduced between opposing electrodes under a pressure in the vicinity of atmospheric pressure, and the material gas is changed into glow discharge plasma by applying a pulsed electric field between the opposing electrodes so that a thin film is formed, in a process of forming a laminated body of a semiconductor element.

[0010] The second invention (the invention of Claim 2) is a manufacturing method of a semiconductor element according to Claim 1, wherein voltage rise time of the pulsed electric field is 100 μs or less, and the field intensity is in a range of 10 to 1000 kV/cm.

[0011] The third invention (the invention of Claim 3) is a manufacturing method of a semiconductor element according to Claim 1 or 2, wherein a solid dielectric is set on an opposing surface of at least one of the opposing electrodes, and a base material is placed between one of the electrodes and the solid dielectric or between the solid dielectrics, so that a thin film is formed on a surface of the base material.

[0012] The fourth invention (the invention of Claim 4) is a manufacturing method of a semiconductor element according to Claim 1 or 2, wherein a solid dielectric vessel provided with a gas outlet is placed on an electrode and an other electrode is provided opposing to the gas outlet, a base material is placed between the gas outlet and the other electrode, and a material gas changed into plasma is discharged continuously from the gas outlet so that a thin film is formed on a surface of the base material.

[0013] The fifth invention (the invention of Claim 5) is a manufacturing method of a semiconductor element according to Claim 1 or 2, wherein a solid dielectric is set on an

opposing surface of at least one of the opposing electrodes, and a material gas changed into plasma is sprayed on a base material between one of the electrodes and the solid dielectric or between the solid dielectrics so that a thin film is formed on a surface of the base material.

[0014] The sixth invention (the invention of Claim 6) is a manufacturing method of a semiconductor element according to Claim 1 or 2, wherein a solid dielectric is set on an opposing surface of at least one of the opposing electrodes, and when a material gas changed into plasma is sprayed on a base material between one of the electrodes and the solid dielectric or between the solid dielectrics, the plasma-state gas is selectively induced to a surface of the base material by applying an electric field to the base material, so that a thin film is formed on the surface of the base material.

[0015] The seventh invention (the invention of Claim 7) is a manufacturing device of a semiconductor element comprising a solid dielectric set on an opposing surface of at least one of opposing electrodes and a base material placed between one of the electrodes and the solid dielectric or between the solid dielectrics, wherein a pulsed electric field is applied between the electrodes.

[0016] The eighth invention (the invention of Claim 8) is a manufacturing device of a semiconductor element comprising a ground electrode provided with a solid dielectric vessel having a gas outlet and an other electrode provided opposing to the gas outlet, wherein a material gas is discharged continuously from the gas outlet, and a pulsed electric field is applied between the ground electrode and the other electrode.

[0017] The ninth invention (the invention of Claim 9) is a manufacturing device of a semiconductor element wherein a solid dielectric is set on an opposing surface of at least one of opposing electrodes and a pulsed electric field is applied between the opposing electrodes, and a material gas changed into plasma is discharged continuously from a gas outlet and sprayed on a base material between one of the electrodes and the solid dielectric or between the solid dielectrics, in a vessel having a gas introducing port and the gas outlet.

[0018] The tenth invention (the invention of Claim 10) is a manufacturing device of a semiconductor element according to any one of Claims 7 to 9, wherein rise time and fall time of a pulsed electric field applied between the electrodes are 100 μs or less, and the field intensity is in a range of 10 to 1000 kV/cm.

[0019]

[Embodiment Mode] Manufacture of a thin film of a semiconductor element of the invention is an atmospheric pressure plasma method in which a material gas is excited and disintegrated using plasma generated by applying a pulsed electric field under a

pressure in the vicinity of atmospheric pressure. In more detail, a method in which a solid dielectric is set on an opposing surface of at least one of opposing electrodes, a base material is placed between the opposing electrodes, and an electric field is applied between the electrodes so that a glow discharge plasma treatment is performed. And a method in which a solid dielectric vessel provided with a gas outlet is placed on an electrode, an electric field is applied between electrodes, and an excited material gas is continuously discharged from the gas outlet so that a base material is treated, and a method in which an excited material gas generated between the electrodes is sprayed on a base material. In addition, it is an atmospheric pressure discharge plasma treatment method and the device characterized in that the electric field to be applied is pulsed, the voltage rise time is 100 μs or less, and the field intensity is in a range of 10 to 1000 kV/cm.

[0020] It is known that a plasma discharge condition is not maintained stably and the transfer to an arc discharge condition occurs quickly with gases other than specific gases such as helium and ketone, under a pressure in the vicinity of atmospheric pressure. However, it is believed that, by applying a pulsed electric field, a cycle in which the discharge is stopped before the transfer to an arc discharge occurs and the discharge is restarted is realized.

[0021] Under a pressure in the vicinity of atmospheric pressure, it is possible that discharge plasma is generated stably in an atmosphere which does not include a component that the time before a plasma discharge condition changes into an arc discharge condition is long such as helium, only when the method of the invention in which a pulsed electric field is applied is used.

[0022] According to the present invention, glow discharge plasma can be generated no matter what kind of gas exists in the plasma generation space. Not only with a known plasma treatment under a low pressure condition but also with an atmospheric pressure plasma treatment under a particular gas atmosphere, it is necessary to perform the treatment in a closed vessel sealed from outside air. However, according to the glow discharge plasma treatment method of the invention, a treatment with an open system, or with a low airtight system which prevents the gas from outflowing freely becomes possible.

[0023] Furthermore, a high-density plasma state can be realized by a treatment under an atmospheric pressure, which is highly significant in performing a manufacture process of a semiconductor element such as a consecutive processing. For realizing the above-described high-density plasma state, two functions which the invention has are related.

[0024] First, a function that gas molecules existing in the plasma generation space are excited effectively by applying a pulsed electric field having precipitous rise whose filed intensity is in a range of 10 to 1000 kV/cm and rise time is 100 μs or less is one of them. Applying a pulsed electric field with slow rise is equivalent to putting energy with different sizes in a phased manner, and molecules which are ionized with low energy, that is, molecules with small first ionizing potential, are excited preferentially first, and next, when higher energy is put, molecules which have been already ionized are excited to a higher level, so that it is difficult to ionize molecules existing in the plasma generation space effectively. On the other hand, according to a pulsed electric field whose rise time is 100 μs or less, energy is given to molecules existing in the space simultaneously, so the absolute number of molecules in an ionized-condition in the space is large, which means the plasma density is high.

[0025] Second, a function that molecules having more electrons than helium, that is, molecules with higher molecular weight than helium are selected as the ambient gas since plasma of a gas atmosphere other than helium can be obtained stably, and as a result, a space with a high electron density is realized. Generally, molecules having more electrons are ionized more easily. As described above, helium is a component which is not ionized easily, but after once ionized, it does not reach arc and exists for a long time in a glow plasma state, therefore it has been used as an ambient gas for atmospheric-pressure plasma. However, as long as the discharge condition is prevented from changing into arc, molecules with larger mass number which are ionized easily are used so that the absolute number of molecules in an ionized-condition in the space can be large and the plasma density can be heightened. With a prior art, it is impossible to generate glow discharge plasma except under an atmosphere where helium exists 90 % or more. Only Japanese Patent Laid-Open Publication No. 4-74525 discloses a technique in which a discharge is performed by sin wave in an atmosphere made of argon and acetone. However, according to the present inventor's additional test, a stable and high-speed treatment cannot be performed at a practical level. In addition, since the atmosphere contains acetone, a treatment except hydrophilic object is disadvantageous.

[0026] As described above, the present invention enables a stable glow discharge under an atmosphere where molecules having more electrons than helium exist excessively, more specifically, under an atmosphere containing compounds with 10 or more of molecular weight at a rate of 10 volume % or more, for the first time, and by this, a high-density plasma state advantageous for a surface treatment is realized.

[0027] "Under a pressure in the vicinity of atmospheric pressure" described above

means under a pressure in a range of $1.333\times10^4$ to $10.664\times10^4$ Pa. Especially, a range of $9.331\times10^4$ to $10.397\times10^4$ Pa where pressure control is easy and the device can be simple is preferable.

[0028] The first plasma treatment method of the invention (the invention of Claim 3) is performed in a device where a pair of opposing electrodes are provided and a solid dielectric is set on at least one of the opposing surfaces of the electrodes. A site where plasma is generated is between the solid dielectric and the electrode in the case where the solid dielectric is set on one of the electrodes, and between the two solid dielectrics in the case where the solid dielectric is set on each of the electrodes. The treatment is performed, placing a base material between the solid dielectric and the electrode or between the two solid dielectrics.

[0029] An example of a device for performing a surface treatment is shown in Fig. 2. In this device, electrode opposing surfaces of an upper electrode 12 and a lower electrode 13 are coated with solid dielectrics, and discharge plasma is generated in a space between the upper electrode 12 and the lower electrode 13. A vessel 10 is provided with a material gas introducing port 16 and a gas exhaust port 19. A material gas is supplied from a material gas supply part 161 through the material gas introducing port 16 to the discharge plasma generation space, and exhausted outside of the vessel 10 from the gas exhaust port 19. In the present treatment, a part which has contact with the generated discharge plasma is treated, so an upper surface of a substance to be treated 15 is treated in the example of Fig. 2. In the case where the both surfaces of the substance to be treated should be treated, the substance to be treated is set floating in the discharge plasma generation space.

[0030] It is preferable that the material gas is supplied uniformly in the plasma generation space. In the device of Fig. 2, the material gas introducing port 16 has a rectifying mechanism of a gas flow, and the gas is exhausted from the gas exhaust port 19, so that the gas flow in the plasma generation space is made uniform.

[0031] As a material for the above-described vessel 10, resin, glass and the like can be used, for example, but not limited to these specially. As long as insulation from the electrode is made, metal such as stainless and aluminum can be used.

[0032] As the above-described electrodes, ones formed of a metal such as copper and aluminum, an alloy such as stainless and brass, an intermetallic compound and the like can be used, for example. The above-described opposing electrodes preferably have a structure in which the distance between the opposing electrodes is roughly constant, to prevent generation of an arc discharge due to electric field concentration. A parallel plate type, a cylindrical opposing plate type, a spherical opposing plate type, hyperbolic

opposing plate type, a coaxial cylindrical structure and the like can be cited as an electrode structure which meets the condition.

[0033] The above-described solid dielectric is set on one of or both of the opposing surfaces of electrodes. At this time, the solid dielectric and the electrode on which the solid dielectric is set are attached firmly to each other, and the opposing surface of the electrode having contact is perfectly covered. Because, when there is some part that is not covered with the solid dielectric so that the electrodes oppose to each other directly, an arc discharge occurs from there.

[0034] The shape of the above-described solid dielectric may be sheet-like, or film-like, and the thickness is preferably in a range of 0.01 to 4 mm. When it is too thick, a high voltage is required to generate discharge plasma, and when it is too thin, a dielectric breakdown occurs when a voltage is applied and accordingly an arc discharge is easily generated.

[0035] As the material of the above-described solid dielectric, for example, plastic such as polytetrafluoroethylene and polyethylene terephthalate, glass, metal oxide such as silicon dioxide, aluminum oxide, zirconium dioxide and titanium dioxide, double oxide such as barium titanate, a bilayer of these and the like can be used.

[0036] Furthermore, the above-described solid dielectric is preferably one with relative dielectric constant of 2 or more (under a 25 °C environment, and hereinafter the same). Polytetrafluoroethylene, glass, a metal oxide film can be cited as specific examples of a dielectric whose relative dielectric constant is 2 or more. Furthermore, to generate high-density discharge plasma stably, it is preferable to use a solid dielectric whose relative dielectric constant is 10 or more. Although the upper limit of the relative dielectric constant is not limited specially, in actual materials, approximately 18,500 are known. As a solid dielectric whose relative dielectric constant is 10 or more, one formed of a metal oxide film in which titanium oxide 5 to 50 % by weight and aluminum oxide 50 to 95 % by weight are mixed, or a metal oxide film containing zirconium oxide is preferable.

[0037] The distance between electrodes described above is decided arbitrarily, considering the thickness of the solid dielectric, the size of the voltage applied, object of using plasma and the like, and it is preferably in a range of 0.1 to 50 mm, and more preferably, 5 mm or less. When it is over 50 mm, it is difficult to generate uniform discharge plasma.

[0038] Furthermore, the second plasma treatment method of the invention (the invention of Claim 4) is a treatment method in which a solid dielectric vessel provided with a gas outlet is set on one electrode (ground electrode), an other electrode is set

opposing to the gas outlet, a base material to be treated is placed between the gas outlet and the other electrode, a material gas is continuously discharged from the gas outlet, and at the same time an electric field is applied between the one electrode and the other electrode so that discharge plasma is generated.

[0039] For example, Fig. 3 is a diagram showing a cross section of an example of a discharge plasma treatment device using an excited gas spurted from between generation electrodes. In Fig. 3, numeral 11 is a power supply, 12 is an applying side electrode, 13 is an other electrode, 14 is a solid dielectric vessel, 15 is a base material to be treated, 16 is a gas introducing port to introduce a material gas into the solid dielectric vessel, 17 is a gas outlet, and 18 is a jig to change the distance between one electrode and the other electrode.

[0040] In a method using a solid dielectric vessel of the invention, discharge plasma is generated in the solid dielectric vessel 14 by applying an electric field between the electrode 12 and the electrode 13 in the state where a material gas is introduced into the solid dielectric vessel 14. The gas in the solid dielectric vessel 14 is spurted from the gas outlet 17 toward the base material to be treated 15, and components of the material gas excited to be in a plasma state have contact with a surface of the base material to be treated 15, so that the base material is treated. Therefore, a treated part of the base material can be changed by changing the relative positions of the solid dielectric vessel 14 and the base material 15, and a treatment of a large-area base material and a treatment of a specified part become possible by a simple device and a small amount of material gas.

[0041] The above-described power supply 11 is made so as to be able to apply a pulsed electric field. By applying a pulsed electric field of the above-described rise time, fall time, and field intensity, a stable discharge condition can be realized under a condition in the vicinity of atmospheric pressure and at low temperature. The detail of such a pulsed electric field will be described later.

[0042] The shapes of the above-described one electrode 12 and other electrode 13 are not limited specially, and they may be curved surface shapes such as cylindrical and spherical, besides the plate shape shown in the figure.

[0043] The distance from the central part of the above-described discharge space to the other electrode 13, through the inside of the solid dielectric vessel 14 and the central part of the gas outlet 17, is decided arbitrarily, according to the wall thickness and material of the solid dielectric vessel 14, the wall thickness and material of the base material 15, the size of a voltage applied and the like, and it is preferably in a range of 0.5 to 30 mm. When it is over 30 mm, a high voltage is required and the discharge

condition easily changes into an arc discharge, so that it becomes difficult to treat the surface uniformly.

[0044] The shape of the solid dielectric vessel 14 used in the invention is not limited specially, and it may be square, cylindrical, spherical and the like, for example.

[0045] The above-described solid dielectric vessel 14 is provided with the one electrode 12. Figs. 4 and 5 are diagrams showing examples of placement of the one electrode and the solid dielectric vessel. In the case where the solid dielectric vessel 14 is square-shaped, the one electrode 12 may be placed on a surface other than the one where a gas outlet 17 is provided. The wall thickness of the solid dielectric vessel 14 surface where the one electrode 12 is placed is preferably in a range of 0.03 to 30 mm. When it is less than 0.03 mm, dielectric breakdown occurs when a high voltage is applied, which sometimes leads to an arc discharge.

[0046] The above-described solid dielectric vessel 14 is provided with the gas introducing port 16 and the gas outlet 17. The shape of the gas outlet 17 is not limited specially, and slit-like one, one formed of many openings, headland-like one formed of a solid dielectric vessel and the like can be cited as the examples. Fig. 6, 7 and 8 are diagrams showing examples of the gas outlet 17.

[0047] Furthermore, as for the solid dielectric vessel of the invention, the solid dielectric vessel itself may have a gas storage capacity, other than one having a gas introducing port shown in Fig. 3.

[0048] The jig 18 of Fig. 3 can change the distance between the other electrode 13 and the gas outlet 17 with complete control. By the jig 18, in the case where the base material to be treated 15 is a large-area substance, the surface treatment can be performed, continuously moving it while keeping the distance between the other electrode 13 and the gas outlet 17 constant, for example. In the case where only a part of the base material 15 is to be treated, a continuous surface treatment, a partial surface treatment and the like can be performed, changing the distance between the other electrode 13 and the gas outlet 17 with complete control. However, when the distance between the gas outlet 17 and the base material to be treated 15 is too long, probability of contacting air increases and the treatment efficiency decreases, so, attention is required.

[0049] Furthermore, the third plasma treatment method of the invention (the invention of Claim 5) is a method in which a solid dielectric is set on an opposing surface of at least one of opposing electrodes, and a material gas excited between one of the electrodes and the solid dielectric or between the solid dielectrics is sprayed on a base material, so that a thin film is formed on the base material surface.

[0050] An example of the device is shown in Fig. 9. In a vessel 10 having a gas introducing port 16 and a gas outlet 17, a solid dielectric is set on at least one opposing surface of opposing electrodes 12 and 12', and a material gas excited between one of the electrodes and the solid dielectric or between the two solid dielectrics is continuously discharged in the direction of the arrow, and sprayed from the gas outlet 17 on the surface of a film-like or plate-like base material 21 moving by rolls, so that a thin film 22 is formed on the base material.

[0051] In the thin film formation by this method, a semiconductor element and the like on which a film is formed is not exposed to the high electric field plasma space directly, and the gas in a plasma state is carried only to the surface, to form the thin film. So, this is a preferable method in which electric and thermal burdens are decreased.

[0052] Furthermore, in the third method of the invention, by putting an electric field to the base material, the gas in a plasma state is induced selectively to the base material surface so that a thin film is formed (the invention of Claim 6). As for the above-described electric field, a pulsed or high-frequency electric field, a continuous wave, a constant electric field load (setting a voltage constant, and the like) and the like can be cited as the examples. For example, a power supply 11 is connected to a base material 21 and a pulsed electric field and the like is applied, as shown in Fig. 10.

[0053] Hereinafter, a pulsed electric field of the invention will be described. An example of a pulse voltage waveform is shown in Fig. 11. Waveforms (a) and (b) are an impulse type, a waveform (c) is a pulse type, and a waveform (d) is a modulation type. Although the voltage apply of repetitions of positive and negative is shown in Fig. 11, a pulse of the type in which a voltage is applied to either positive or negative polarity side may be used. Furthermore, a pulsed electric field where a direct current is superimposed may be applied. The waveform of a pulsed electric field of the invention is not limited to the ones described here, and modulation may be performed using pulses with different pulse waveforms, rise time and frequency. The above-described modulation is suitable for performing a high-speed continuous surface treatment.

[0054] The rise and fall time of the above-described pulsed electric field is 100 μs or less, and preferably 10 μs or less. When it is over 100 μs, the discharge condition becomes unstable, easily changing into arc, and it becomes difficult to obtain a high-density plasma state by a pulsed electric field. In addition, the shorter the rise time and the fall time are, the more efficiently ionization of the gas when plasma is generated occurs. However, it is difficult to realize a pulsed electric field whose rise time is less than 40 ns. More preferably, it is in a range of 50 ns to 5 μs. Here, rise

time means the time when a voltage (absolute value) continuously increases, and fall time means the time when a voltage (absolute value) continuously decreases.

[0055] Furthermore, the fall time of the pulsed electric field is preferably precipitous, and in the same way as the rise time, it is preferably a time scale of 100 μs or less. Although it differs depending on a pulsed electric field generation technique, the rise time and the fall time can be set as the same time, in the case of the power unit used in the embodiment of the invention, for example.

[0056] The field intensity of the above-described pulsed electric field is in a range of 10 to 1000 kV/cm, and preferably in a range of 20 to 300 kV/cm. When the field intensity is less than 10 kV/cm, too much time is required for the treatment, and when it is over 1000 kV/cm, an arc discharge is easily generated.

[0057] The frequency of the above-described pulsed electric field is preferably 0.5 kHz or more. When it is less than 0.5 kHz, too much time is required for the treatment since the plasma density is low. The upper limit is not limited specially, and high frequency zone such as 13.56 MHz which is regularly used and 500 MHz which is used on a trial bases is all right. Considering obtaining load matching easily and handling, 500 kHz or less is preferable. By applying a pulsed electric field like this, the treatment speed can be greatly improved.

[0058] Furthermore, one pulse duration in the above-described pulsed electric field is preferably 200 μs or less, and more preferably in a range of 3 to 200 μs. When it is over 200 μs, it becomes easy to change into an arc discharge. Here, one pulse duration means a continuous ON time of one pulse in a pulsed electric field made of repetitions of ON and OFF, as shown with the example in Fig. 11.

[0059] Due to the characteristics above, the device of the invention can perform thin film formation such as electrode formation, interlayer insulating film formation, passivating film (protective film) formation and Si-film formation on a substrate respectively, by changing the gas kind, electric field condition, film formation environment and the like, when manufacturing a semiconductor element.

[0060] For example, as a material gas for forming an electrode film, a material gas of a metal-hydrogen compound, a metal-halogen compound, a metal alkyl compound and the like of metals such as Al, Cu, Si, Ti and Sn, an organic aluminum compound gas or the like, for example, can be used so as to form a metal film. In addition, for a metal oxide thin film such as an interlayer insulating film, a material gas of a metal-hydrogen compound, a metal-halogen compound, an alkyl metal compound and the like with oxygen or an alcoholate gas can be used so as to form a metal oxide thin film such as $SiO_2$, $TiO_2$ and $SnO_2$. For a passivating film as the last insulating film of interlayer

insulating films, a gas which mainly forms a silicon nitride film, such as a slane-series gas and a nitrogen-containing gas, for example, can be used so as to form an $Si_3N_4$ film and the like. Furthermore, for an Si-series film, an Si-hydrogen-series gas, an Si-halogen-series gas, an Si-fluorine-series gas, such as silane, disilane and the like for example, can be used so as to form a thin film such as an amorphous Si film, a poly-Si film and an Si-C film. By mixing an impurity gas such as $GeH_4$, $AsH_3$ and $B_2H_6$ with a silane-series gas, a thin film of an amorphous Si layer doped with P, B, As, Ge and the like can be formed.

[0061] Furthermore, electric and optical functions can be added to the base material surface. Especially, film formation of an interlayer insulator, a passivating film and the like can be applied to an IC circuit, a solar cell, a switch of a liquid crystal display, and other semiconductor devices.

[0062] From a standpoint of economy, safety and the like, the treatment is preferably performed in an atmosphere where the material gas is diluted by an inert gas. As the inert gas, for example, a noble gas such as neon, argon and xenon, or a nitrogen gas and the like may be used. They can be used separately, or two or more kinds of them may be mixed and used. Conventionally, a treatment under a pressure in the vicinity of atmospheric pressure is performed in the presence of helium. However, according to the method of the invention in which a pulsed electric field is applied, a stable treatment in an argon or nitrogen gas which are less expensive than helium is possible, as described above.

[0063] Conventionally, under a pressure in the vicinity of atmospheric pressure, a treatment is performed under an atmosphere where helium exists excessively. However, according to the method of the invention, a stable treatment in argon or a nitrogen gas which are less expensive than helium is possible. Furthermore, by performing the treatment in the presence of such gases with high molecular weight, having more electrons, a high-density plasma state is realized and the treatment speed can be increased, which provides great industrial advantages.

[0064] The mixing ratio of a material gas and an inert gas is decided arbitrarily by the gas kind. When concentration of the material gas is too high, extra reactions not contributing to the film formation easily occur. Therefore, the concentration of a material gas is preferably in a range of 0.001 to 10 volume %, and more preferably in a range of 0.001 to 0.5 volume %.

[0065] With the atmospheric pressure discharge using a pulsed electric field of the invention, it is possible to generate a discharge directly in an atmospheric pressure between electrodes, not depending on the gas kind at all, and a high-speed treatment can

be realized by the atmospheric pressure plasma device with the more simplified electrode structure and discharge procedure, and by the treatment method. In addition, by parameters of the pulse frequency, voltage, distance between electrodes and the like, semiconductor element treatment parameters for each thin film can be controlled. Furthermore, selective excitation is possible by frequency control including the shape of a pulsed electric field applied and modulation, and it is possible to selectively improve the film formation speed of a specified compound, or to control the purity of an impurity and the like.

[0066] Although a glow discharge plasma treatment of the invention may be performed heating or cooling a base material, it is fully possible at room temperature, and its ability of treating at lower temperature than a film forming temperature of a conventional method characterizes the invention. The time required for the above-described glow discharge plasma treatment is decided arbitrarily, considering the applied voltage, the material gas kind and its proportion in the mixture gas, and the like.

[0067]

[Embodiment] Hereinafter, the invention will be described specifically, but the invention is not limited to these embodiments.

[0068] Embodiment 1

Parallel plate electrodes shown in Fig. 9 are used. Alumina as a solid dielectric is sprayed to a thickness of 1 mm on an electrode 12 (made of stainless (SUS304), width 300 mm × length 100 mm × thickness 20 mm) and an electrode 12' (made of stainless (SUS304), width 300 mm × length 100 mm × thickness 20 mm). The electrodes are set parallel with a space of 2 mm therebetween, and a polyimide film (size: 100 × 100 mm, thickness: 50 μm) is set as a base material on which a film is formed in a position 5 mm away from an outlet.

[0069] Exhaust is performed by an oil-sealed rotary pump until the inside of the device becomes $1.333 \times 10^2$ Pa. Next, after the inside of the device is made to be $10.13 \times 10^4$ Pa by an argon gas, a mixed gas made by diluting silane 0.1 % and hydrogen 1 % with an argon gas is introduced into the device from an introducing tube 16, as a material gas. Using the pulse shape of Fig. 11 (a) between the electrode 12 and 12', film formation is performed under the conditions of pulse rise speed 5 μs, frequency 10 kHz, voltage Vpp 20 kV and 95 kPa, then generation of an amorphous Si thin film is seen on a film. The firm forming speed at this time is 30 nm/min.

[0079] Comparative Example 1

In Embodiment 1, using a sine wave of 150 MHz as an electric field applied, using helium as a carrier gas, using silane 0.1 % and hydrogen 1 % mixed as a material gas,

and setting other conditions the same as the embodiment, an amorphous Si thin film is formed on a polyimide film. Generation of the amorphous Si thin film can be seen, but the film forming speed is 6 nm/min.

[0071] Comparative Example 2

Using the device of Fig. 9, inline film formation is performed. Electrodes coated with a solid dielectric are set parallel with a space of 2 mm therebetween, an argon gas with TEOS 0.3 % and oxygen 20 % mixed in is used as a material gas, a pulsed electric field is applied under the same conditions as Embodiment 1, and the material gas in a plasma state is sprayed on a stainless base material from a gas outlet 17. As a result, an $SiO_2$ film is formed on a base material, and the film forming speed is 100 nm/min.

[0072]

[Effect of the Invention] According to a manufacturing method of a semiconductor element of the invention in which a pulsed electric field is applied, uniform discharge plasma can be generated stably under a pressure in the vicinity of atmospheric pressure, regardless of gas atmosphere. Therefore, all thin films required for a semiconductor element, such as an electrode, an interlayer insulator, a passivating film, and an Si film, can be formed easily. In addition, the method of the invention can reduce the cost of equipment, compared to a conventional low pressure method. Furthermore, a low cost gas such as argon and a nitrogen gas can be used, instead of a high cost gas such as helium. In addition, high speed productivity can be achieved since high speed film formation by high-density plasma is possible, and a high-level treatment in a short time is possible, especially a treatment at low temperature is possible, which has great significance for performing industrial processes such as a high speed continuous treatment.

[Brief Description of the Drawings]

Fig. 1 is a diagram describing a structure of a semiconductor element.

Fig. 2 is a cross-sectional view showing an example of a discharge plasma treatment device of the invention.

Fig. 3 is a cross-sectional view showing another example of a discharge plasma treatment device of the invention.

Fig. 4 is a diagram of an example of arrangement of a solid dielectric vessel and one electrode of a discharge plasma treatment device.

Fig. 5 is a diagram of an example of arrangement of a solid dielectric vessel and one electrode of a discharge plasma treatment device.

Fig. 6 is a diagram of an example of a gas outlet of a discharge plasma treatment device.

Fig. 7 is a diagram of an example of a gas outlet of a discharge plasma treatment device.

Fig. 8 is a diagram of an example of a gas outlet of a discharge plasma treatment device.

Fig. 9 is a diagram of an example of a gas blowing discharge plasma treatment device.

Fig. 10 is a diagram of an example of a gas blowing discharge plasma treatment device.

Fig. 11 is a voltage waveform diagram showing an example of a pulsed electric field of the invention.

[Description of Numerals]

1: substrate
2: silicon film
3: source electrode
4: drain electrode
5: interlayer insulator
6: gate electrode
7: passivating film
10: vessel
11: power supply
12: upper electrode
13: lower electrode
14: solid dielectric vessel
15: substance to be treated
16: material gas introducing port
161: material gas supply part
17: gas outlet
18: jig
19: gas exhaust port
21: substrate
22: thin film

Continued from the front page
(51) Int. Cl.$^7$: C23C 16/517, H01L 31/04, H05H 1/46
Identification Mark
FI: C23C 16/517, H05H 1/46, H01L 31/04

Theme Code (reference): M, V

F term (reference): 4G075, AA24, BC04, BD03, CA16, CA47
CA63, DA01, DA02, DA18, EB01
EB42, EC21, ED11, FC15
4K030, AA06, AA09, AA14, AA16, AA17
BA30, BA44, CA02, CA07, CA17
FA01, FA03, GA14, HA07, JA09
JA11, JA14, KA08, KA14, KA30
KA32, KA46, LA12, LA15, LA16
5F045, AA08, AB04, AB32, AC01, AC07
AC11, AC16, AE29, DP22, EH04
EH08, EH13, EH19
5F051, AA05, CA15, CA23, CA35, CA40
GA03, GA05